MTBE Remediation

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Overview

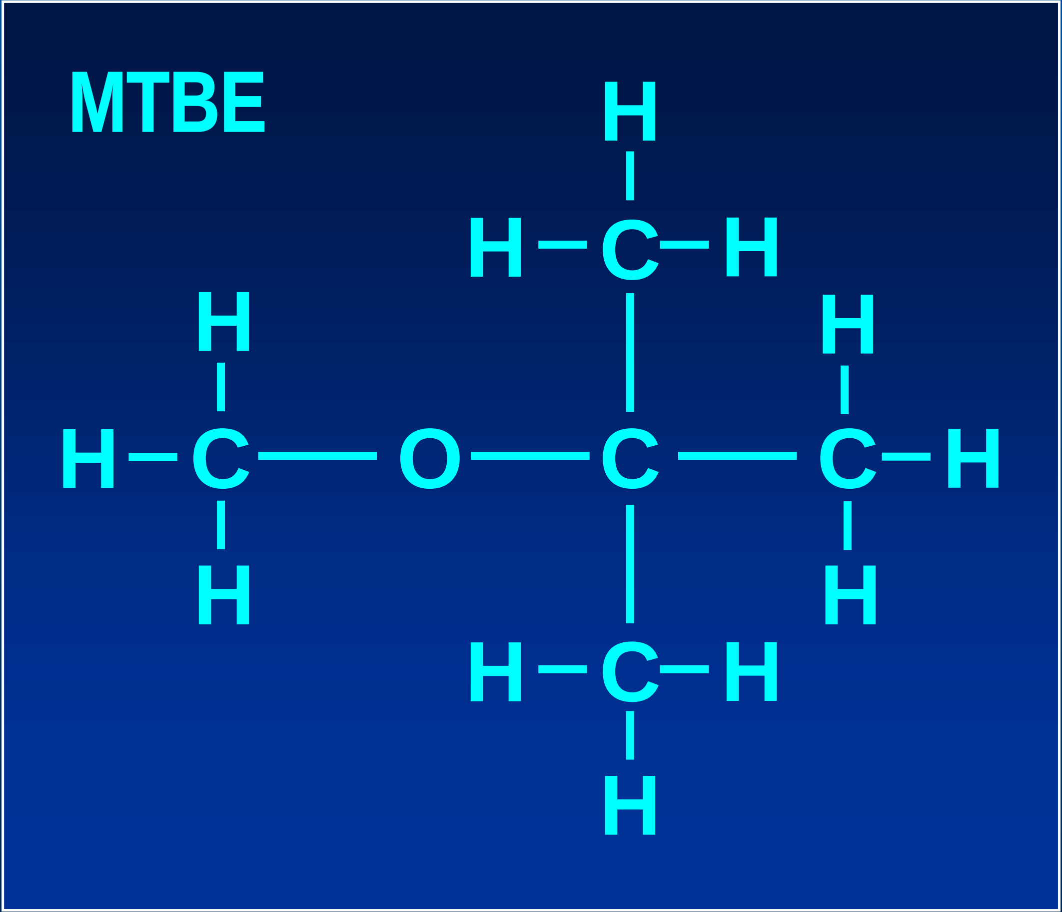
- Definitions and Facts
- Current Regulatory Positions
- Traditional Remediation Technologies
- Innovative Remediation Technologies
- Conclusions
- Case Studies

Definitions and Facts

- MTBE: Methyl tertiary butyl ether, an oxygen-containing gasoline additive
- Used in the United States since 1979; usage increased steadily in 1980s, then dramatically in 1990s
- MTBE is the most commonly used gasoline additive and is the second most manufactured chemical
- MTBE usage in gasoline:
  - 0 to 8% (volume/volume) for octane boosting
  - 11% in select wintertime gasoline since 1988
  - 15% in Federal Oxy-fuel since 1992
  - 11% in Federal reformulated gasoline (RFG) since 1995

MTBE Molecule

- Methyl tertiary butyl ether



Properties: Benzene vs. MTBE

Property	Benzene	MTBE
Volume % in gasoline	1-3%	0-15%
Pure compound solubility (mg/L)	1,780	50,000
Typical maximum conc. in water (mg/L)	65	400
Vapor pressure (mm Hg)	95	245
Henry’s law constant	0.22	0.02
Affinity for organic carbon (Log K_{oc})	2	1.05
Taste threshold in water (µg/L)	~ 500	5-40
Natural biodegradability	High	Low

MTBE Detections in Groundwater near Leaking Underground Storage Tank (LUST) Sites

State	# LUST Sites Tested	# LUST Sites with MTBE	% LUST Sites with MTBE
California	6,127	4,595	75%
Texas	609	566	93%
Kansas	929	818	88%

Using 1995-1998 groundwater analyses

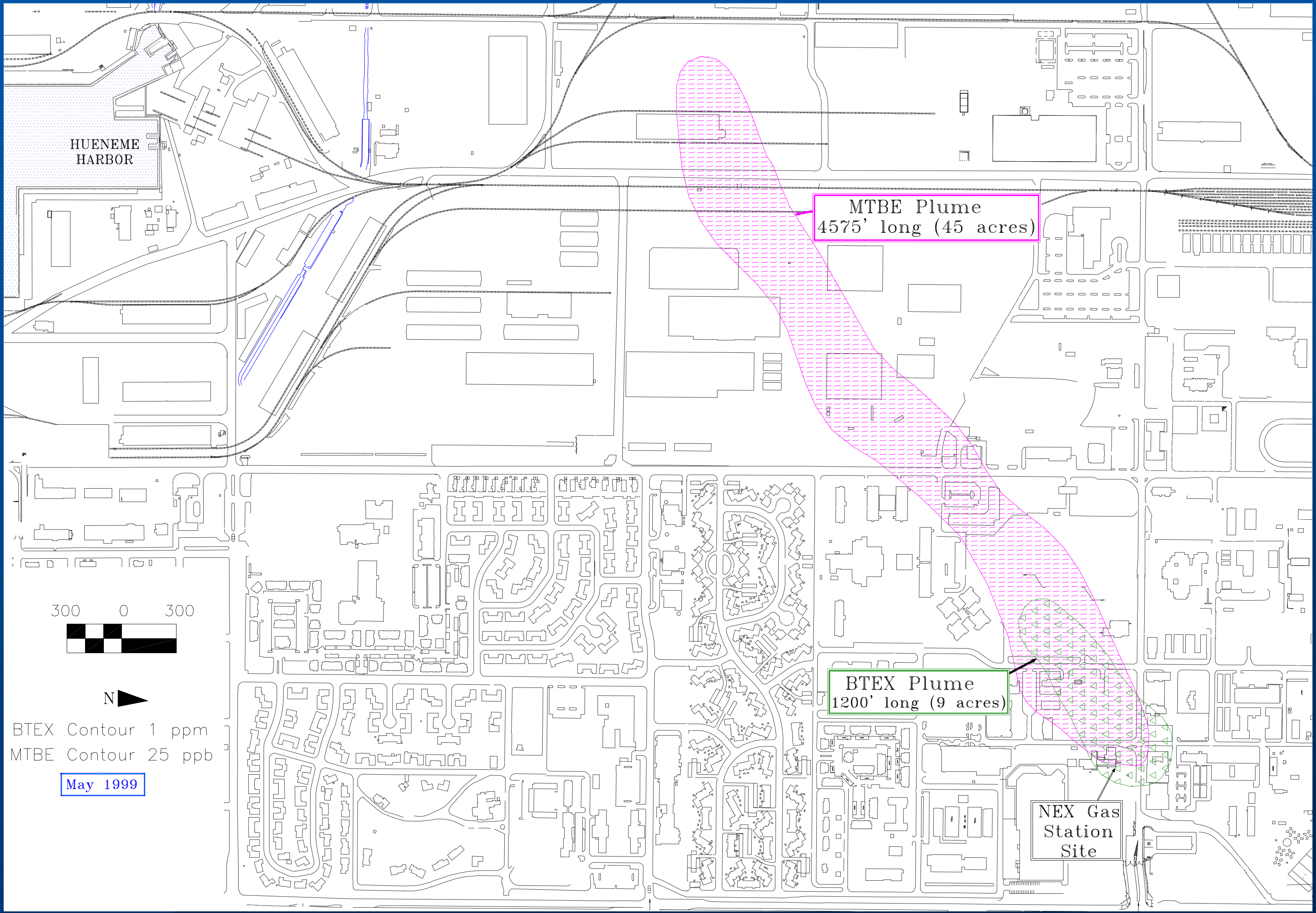
More MTBE Facts

- MTBE sometimes found in jet fuel and #2 heating oil (cross-contamination during transport and storage)
- MTBE in water has low taste and odor thresholds (about 20 to 40 µg/L)
- Nationwide:
  - 5% to 10% of drinking water wells in RFG/Oxy-fuel areas contain detectable levels of MTBE
  - 99% of those MTBE detections are < 20 µg/L
- State-specific examples:
  - In CA, 62 of 6,409 drinking water sources (<1%) tested contained MTBE; Santa Monica, CA wells contained up to 600 µg/L
  - In La Crosse, KS, the sole-source public well field contained 600 µg/L

Subsurface Characteristics of MTBE

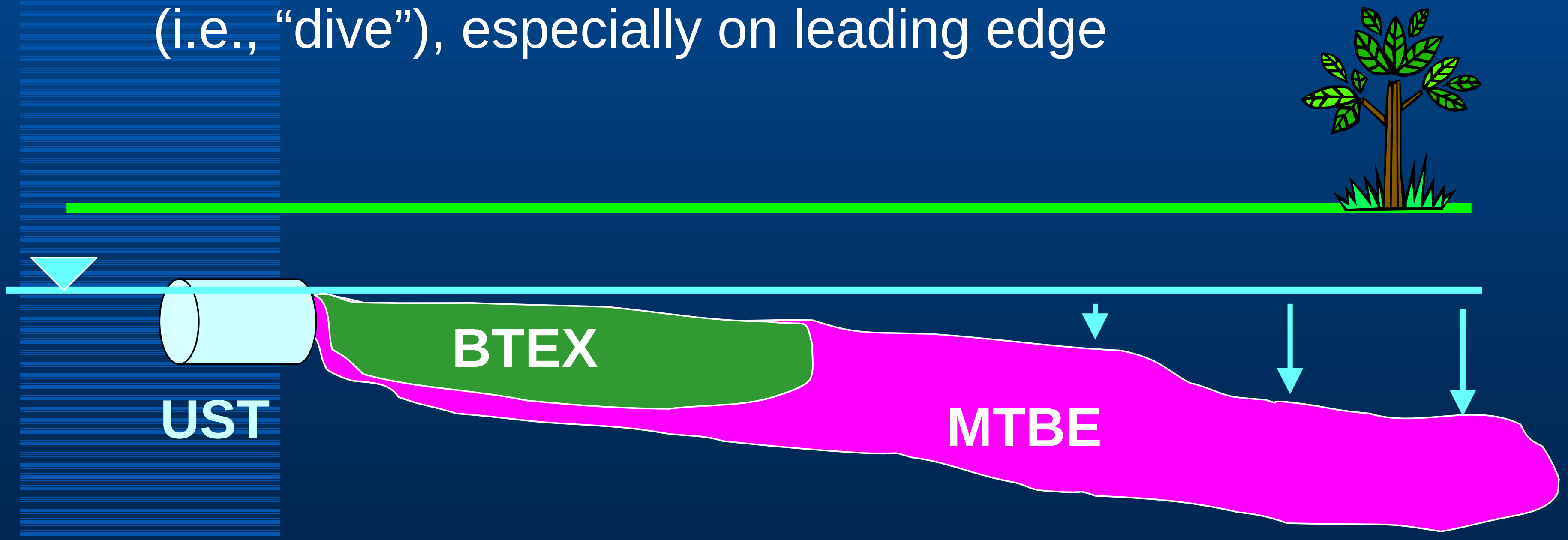
- 28 times more soluble than benzene
- 10 times less volatile from water than benzene
- Much less retarded than benzene
- Much less biodegradable than benzene

Port Hueneme, CA – MTBE & BTEX Plumes



Movement of MTBE Plumes

- MTBE plumes move faster than BTEX compounds
- MTBE plumes move farther than BTEX compounds
- MTBE plumes occasionally source-separate, or detach
- MTBE plumes sometimes extend deeper into aquifers (i.e., “dive”), especially on leading edge



Factors that Increase MTBE Vertical Transport

- With greater longitudinal transport, the total vertical dispersion increases (minor)
- With greater plume length, there is more downward slug displacement from numerous infiltration events
- Greater plume length means MTBE plume is more likely to encounter a pumping well (which can rapidly pull down any dissolved-phase compound)
- Greater plume length means the MTBE plume is more likely to encounter a geologic layer that allows downward migration (i.e., greater heterogeneity over larger scale)

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Recent Water Standards for MTBE

Locale (Year)	MTBE Standard (µg/L)	Type of Water Standard
Federal (1998)	20-40	Health advisory (HA) for taste and odor; nonenforceable
California (1999)	13 – MCL (expected) 5 – SMCL	Drinking water; enforceable
New York (1999)	10	"Guidance criteria" enforceable for all waters; stringent!
25 states have standards (from 10 to 200 µg/L), 8 states are developing standards, 4 use site-specific levels, and 13 use the current Federal HA and/or are waiting for the Federal maximum contaminant level (MCL) (a 5- to-10-year wait)		

For a national map with updated MTBE regulations: www.epa.gov/swerust1/mtbe/MTBEmap.htm

Cleanup Levels

- If no one is consuming MTBE-impacted water, drinking-water standards may be inappropriate.
- Site-specific, risk-based levels for MTBE needed; reference doses and slope factors are being developed.
- Low taste and odor thresholds, continued movement, liability, and perceptions all factor in.
- Navy: no Preliminary Remediation Goal (PRG)…funding issue?

Additional Regulatory Activity

- U.S. Environmental Protection Agency (EPA) Blue Ribbon Panel recently issued a report that advised “the use of MTBE should be reduced substantially” (to phase-out with minimal disruptions and costs over 4 years)
- California banned MTBE use after December 2002
- A 1999 New England study advised a three-year phase down and cap on MTBE
- Several states (CA, ME, and NH) and non-attainment (air quality) areas trying to get out of the Federal RFG and Oxy-fuel programs, mostly to help avoid MTBE… Congressional action is needed, however!
- Other state studies currently are underway

MTBE Litigation

- Class-action lawsuits over MTBE usage have been filed against oil companies, gasoline distributors, and MTBE manufacturers (even industry representative groups) in:
  - Maine
  - North Carolina
  - New York
  - California (two)
- Site-specific lawsuits have been filed in California by impacted water utilities (Santa Monica and South Lake Tahoe)
- More to come?

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Traditional Remediation Technologies:
Technology Progression

Contaminant	Stage	Technology
Petroleum Hydrocarbons	Conventional	Biopile
		Composting
		Land Farming
		Bioslurry Reactors
		Bioventing
		Bioslurping
	Innovative	Air Sparging
		Monitored Natural Attenuation (Petroleum Hydrocarbons)
Chlorinated Hydrocarbons		Monitored Natural Attenuation (Chlorinated Hydrocarbons)
	Emerging	Enhanced Anaerobic Dechlorination (EAD)
		Anaerobic Bioventing
		Sequential Anaerobic/Aerobic Treatment
		In Situ Cometabolism
		Cometabolic Air Sparging (CAS)
	Early Development	Bioaugmentation
		Bioengineering (GEMs)

Traditional Remediation Technologies

- Many technologies that work for remediating gasoline also will work for MTBE
- However, most technologies will be less effective and/or more costly for MTBE
- Traditional technologies include:
  - Risk-based corrective action (RBCA)
  - Soil excavation
  - Air sparging (AS)
  - Soil vapor extraction (SVE)
  - Bioventing
  - Groundwater (GW) extraction (and water treatment)

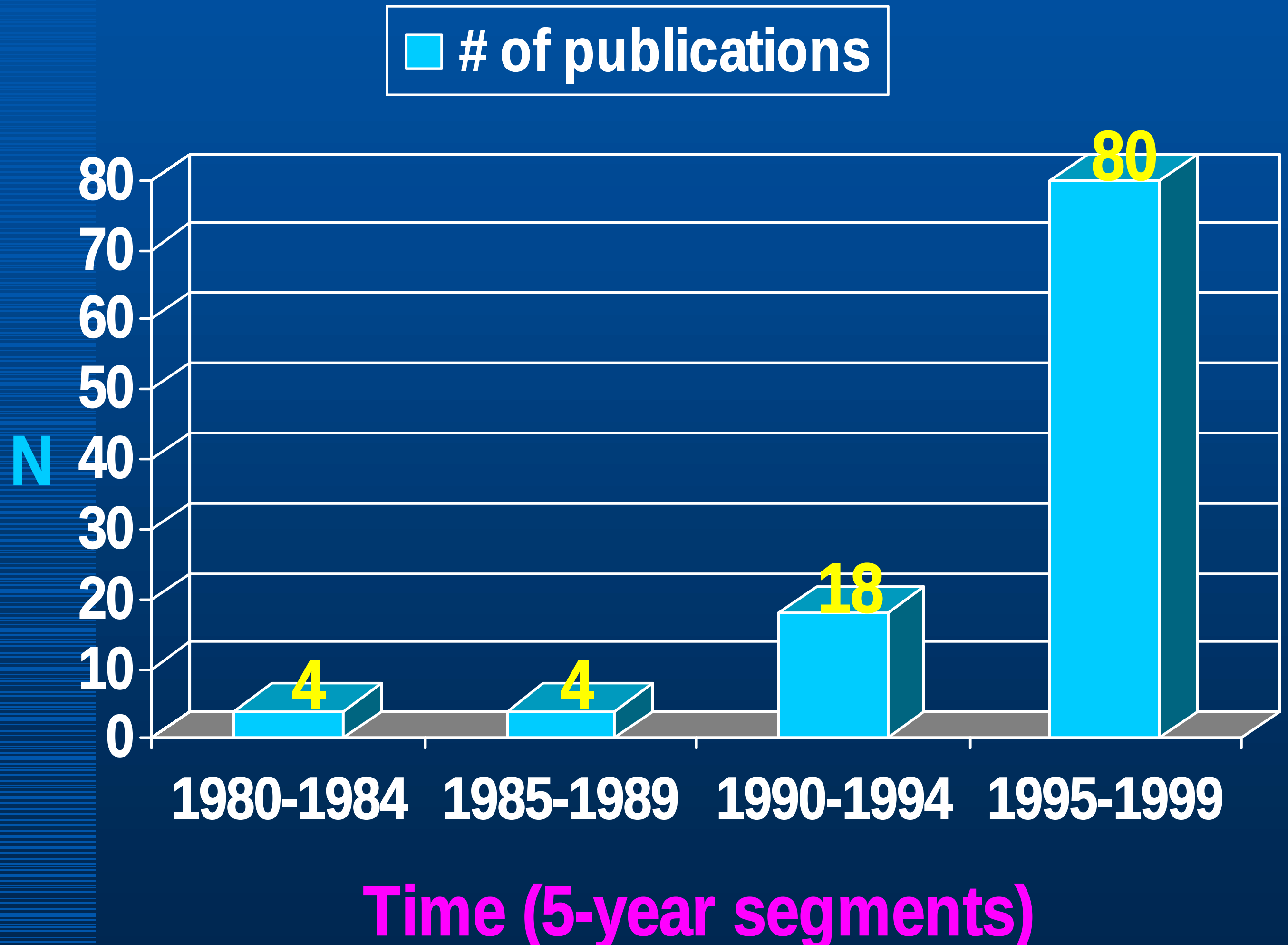
Traditional Remediation Technologies –
Good Performers

Technology	Applicability for MTBE	Reported Field Applications	Performance and Comments
RBCA approach	Fully Applicable	Few	Process works fine, but results may be unfavorable for MTBE
SVE	Very applicable if applied soon; poor if applied later	Dozens	MTBE's high vapor pressure makes SVE excellent initially; but only before MTBE leaches into GW
Groundwater extraction	Plume control is very good	Dozens	P&T is great for hydraulic containment; still limited by residual product & hydrogeo.
	Remediation is good for dissolved phase	Dozens	Better for soluble MTBE than for most compounds

Traditional Remediation Technologies – Poor Performers

Technology	Applicability for MTBE	Reported Field Applications	Performance and Comments
Soil excavation	Variable with time	Few	If implemented soon after spill, can be effective; if implemented later, when the MTBE is leached from soil, is ineffective
Air sparging	Variable, still being determined	> 12	Aeration benefit reduced (hard to "strip") and biodegradation benefit much reduced; field results mixed from good to very poor
Bioventing	Not promising so far	3-4	Performance poor; so far control areas show no measurable improvement

MTBE Remediation and Treatment: An Emerging Issue



Aboveground Treatment of MTBE-Impacted Water

Technology	Theoretical Effectiveness on MTBE	Development Level	Performance and Comments
Air stripping	Good-fair	Field: many good applications	Higher air/water ratio needed, air emissions problematic
Carbon adsorption	Good in select situations	Field: some good applications, many poor ones	High granular activated carbon (GAC) usage (rapid breakthrough possible); virgin coconut GAC best
Advanced oxidation processes	Good	Pilot: looks promising; field studies starting	Destroys MTBE; high capital costs; byproducts can be problematic
Resin sorbents	Good; effective on tertiary-butyl alcohol (TBA)	Lab: pilot test starting	Looks promising, especially if TBA present and of concern; high capital costs

See CA MTBE Research Partnership (2000) for details and costs

Cost of MTBE Remediation

- The added cost of remediating a gasoline spill site when MTBE is present varies widely:
  - If active remediation ongoing, a little MTBE arrives, and no system changes needed ➔ little to no cost increase
  - If active remediation ongoing, MTBE arrives, and system changes or expansion needed ➔ moderate cost increase
  - If active remediation <u>not</u> occurring, MTBE arrives, and a new remedial method needed (i.e., change from passive to active) ➔ major cost increase

Cost of MTBE Remediation

- Cost of treating MTBE-impacted water is 40% to 80% more than treating BTEX-impacted water (Keller et al., 1999)
- Survey of early MTBE experience in RFG states (Hitzig et al., 1998) concluded that:
  - At 60% of LUST sites, cost increases are 0-20%
  - At 32% of LUST sites, cost increases are 20-100%
  - At 8% of LUST sites, cost increases are >100%
- MTBE may cause active remediation costs to increase 20-80% at most sites, and occasionally significantly more
- “Hot spot” reduction, a quick response, and/or using alternative cleanup goals can greatly reduce scale of project, thus saving considerable money

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Innovative Remediation Technologies:
Phytoremediation

- Technology Description:
  - Involves using plants and trees to decontaminate subsurface; for MTBE, this involves mass removal to control downgradient spread of dissolved-phase MTBE
  - Mature trees can passively “pump” (evapotranspire) several hundred gallons of water per day from subsurface
  - Cores of live oak trees above a plume showed MTBE in the tree fluids
  - Being tested at Port Hueneme
  - Looks promising, but…

Innovative Remediation Technologies:
Phytoremediation

- Applicability limited because:
  - Can’t use if plume ill-defined
  - Trees must be mature, located at correct locales, and sufficient in number
  - If GW velocity more than 10 ft/yr, insufficient “treatment”
  - MTBE plume may be “diving” below root zone
  - Still much to learn

Innovative Remediation Technologies:
In Situ Chemical Oxidation

- Can destroy MTBE in place
- Common method is by inducing a Fenton's Reaction, in which hydroxyl radicals (OH• groups) are created in the ground
- Requires injection of ozone, H_2O_2, or both
- Some byproducts created
- Field tests ongoing at MTBE sites
- Technology still developing

Innovative Remediation Technologies:
Enhanced Biodegradation

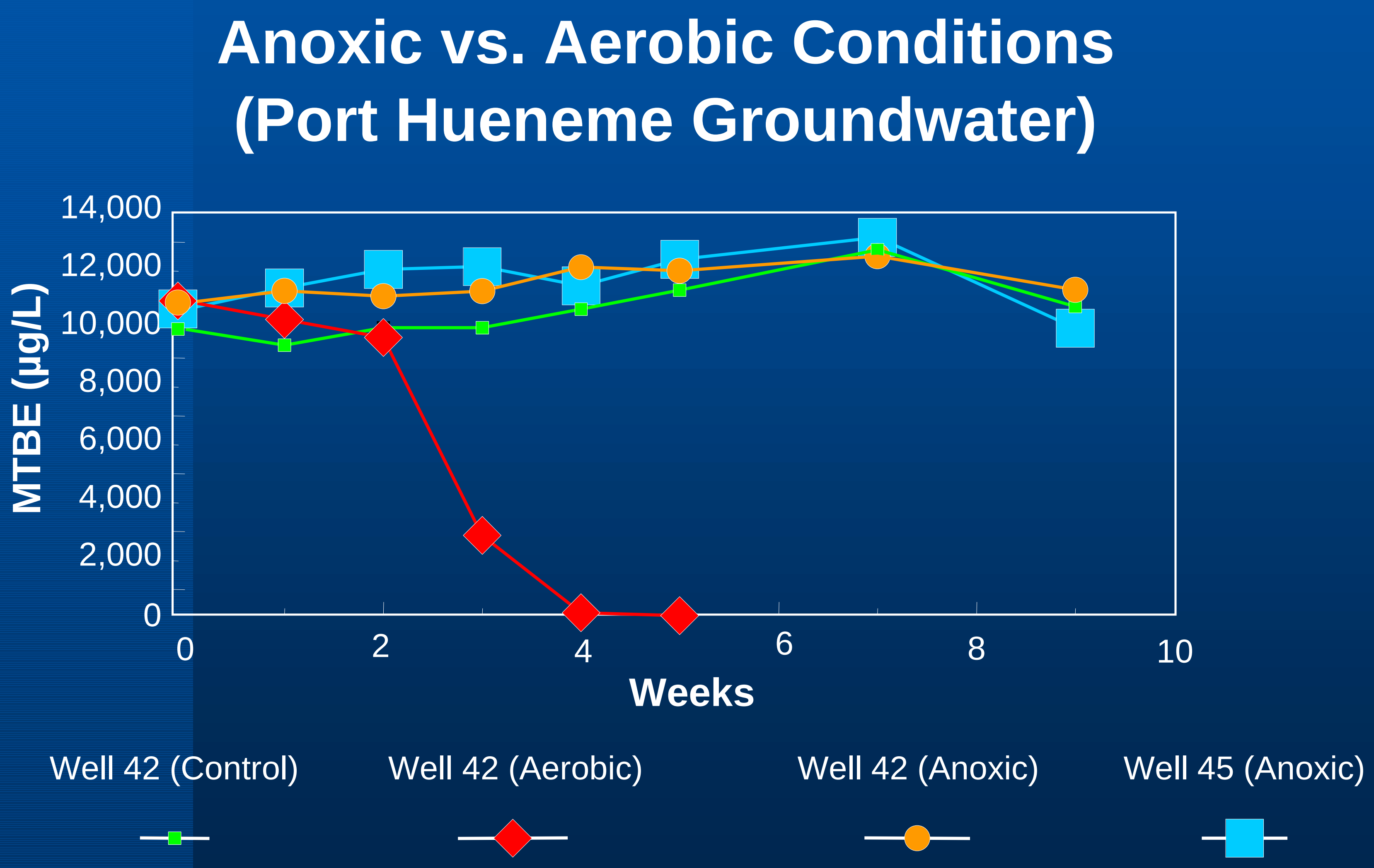
- Most promising innovative process for MTBE
- Multiple methodologies and microbial consortium being developed
- LOTS of work going on

Why is MTBE Difficult to Biodegrade?

Aquifer Factors	Property/Finding
MTBE molecule	• Ether and tertiary carbon bond recalcitrance
Cell growth	• Slow growth (0.05/d) • Low yield (0.1 to 0.2 g-cells/g-MTBE) • Low #'s of indigenous degraders (0.001% of total population in biotreaters)
Metabolism	• MTBE>TBA>IPA>Acetone>Pyruvate>Acetate
MTBE-degrading activity	• Most cultures are aerobic • Affected by low dissolved oxygen (DO), other VOCs, pH, and/or temperature
Aquifer activity	• Low #'s degraders/L-GW or g-soil (0-100) • Plume enrichment (degraders) very slow (field natural attenuation rate, 0.001/d)

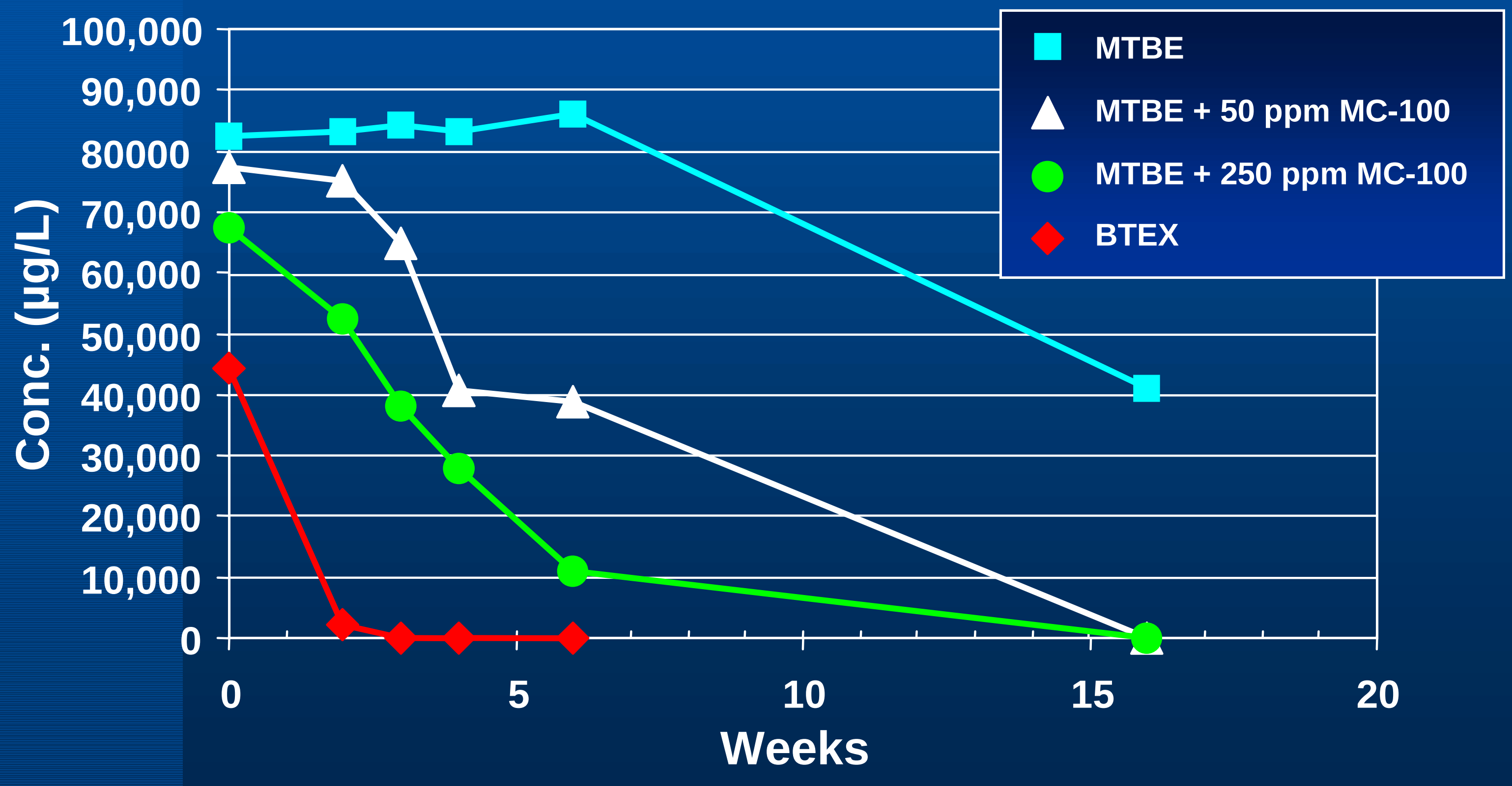
Slides adapted from those of Joe Salanitro & Equilon Enterprises

Experimental Microcosms
No Microbial Cultures Added

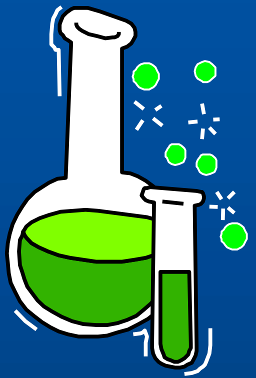


Experimental Microcosms
Microbial Cultures Added

Biodegradation of BTEX and MTBE in Port Hueneme Aquifer Soil
(700 ppm gasoline)



Comparison of MTBE-Degrading Cultures



Investigator	Culture	Feature
1. Hardison *(OSU)*	Graphium	cometabolic (butane)
2. Hyman *(NCSU)*	n/br-alkane-oxidizers	cometabolic (n/iso-C_3-C_6)
3. Steffan *(Envirogen)*	propane-oxidizers	cometabolic (propane)
4. Corcho/Watkinson *(Shell International)*	cyclohexane-oxidizers	cometabolic (cyclohexane)
5. Mahaffey *(Pelorus)*	aromatic-oxidizers	cometabolic (benzene)
6. Mo et al. *(Notre Dame)*	Methylobacterium, Rhodoccoccus, Arthrobacter	slow growth on MTBE
7. Hanson/Scow *(UC-Davis)*	Sphingomonas	low cell yields on MTBE
8. Fortin/Deshusses *(UC-Riverside)*	mixed (municipal)	low cell yields on MTBE
9. Park/Cowan *(Rutgers)*	mixed (refinery biosolids)	low cell yields on MTBE
10. Salanitro *(Equilon)*	mixed (chemical biosolids)	low cell yields on MTBE
	Rhodococcus	MTBE degradation inducible

Enhanced Bioremediation – The Good News

- Once BTEX and other hydrocarbons are gone, MTBE degradation increases
- Numerous MTBE-degrading cultures have been identified; lab tests indicate that adding these cultures clearly enhances MTBE biodegradation rates in microcosms
- Adding DO also helps
- Adding a microbial consortia and oxygen together increases degradation rates even more

Enhanced Bioremediation – The Good News

- Several field tests have shown good success:
  - Port Hueneme w/Equilon’s MC-100, BC-4, UC-Davis cultures
  - At three sites (WI, CA, and MI), oxygen added by oxygen release compound (ORC) emplacement seemed to increase MTBE biodegradation rates by indigenous microbes and/or produced TBA from MTBE (be careful…)
  - An engineered system at Vandenberg Air Force Base (AFB) is successfully degrading MTBE with an injection of non-native microbes and oxygen
  - In CT, a vigorous closed-loop circulation of enzymes, pure oxygen, and nutrients reduced BTEX and MTBE levels by 97% in 34 days; site bioremediated in 18 months

Enhanced Bioremediation – The Bad News

- Natural MTBE biodegradation rates are about 1/20th that of benzene
- MTBE does not degrade well in the presence of more readily consumed compounds like BTEX
- To enhance natural MTBE degradation, we may have to promote BTEX biodegradation, or wait for sequential degradation

Enhanced Bioremediation – The Bad News

- Lab and field results are still quite mixed: MTBE not seen to be biodegrading everywhere, all the time
- Even the favorable results cannot all be explained
- For large, dilute plumes, the MTBE concentrations may be too low to support rapid bioactivity
- Enhancing MTBE biodegradation may help a lot, but it is still expected to be a slow process at most sites

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Conclusions

- Increasing regulatory and litigation activity indicates that MTBE contamination likely to become a bigger concern
- Be attentive when defining MTBE plumes (they can move fast and far; they can dive)
- Most traditional technologies are applicable to MTBE, though often less effective than for BTEX compounds
- Many MTBE plumes will be more difficult or more costly to remediate than BTEX plumes

Conclusions (Cont.)

- MTBE may cause active remediation costs to increase 20-80% at many sites, and even significantly more at some sites
- Field experience has shown that subsurface MTBE can be remediated and treated
- Several innovative technologies look promising, especially enhanced bioremediation

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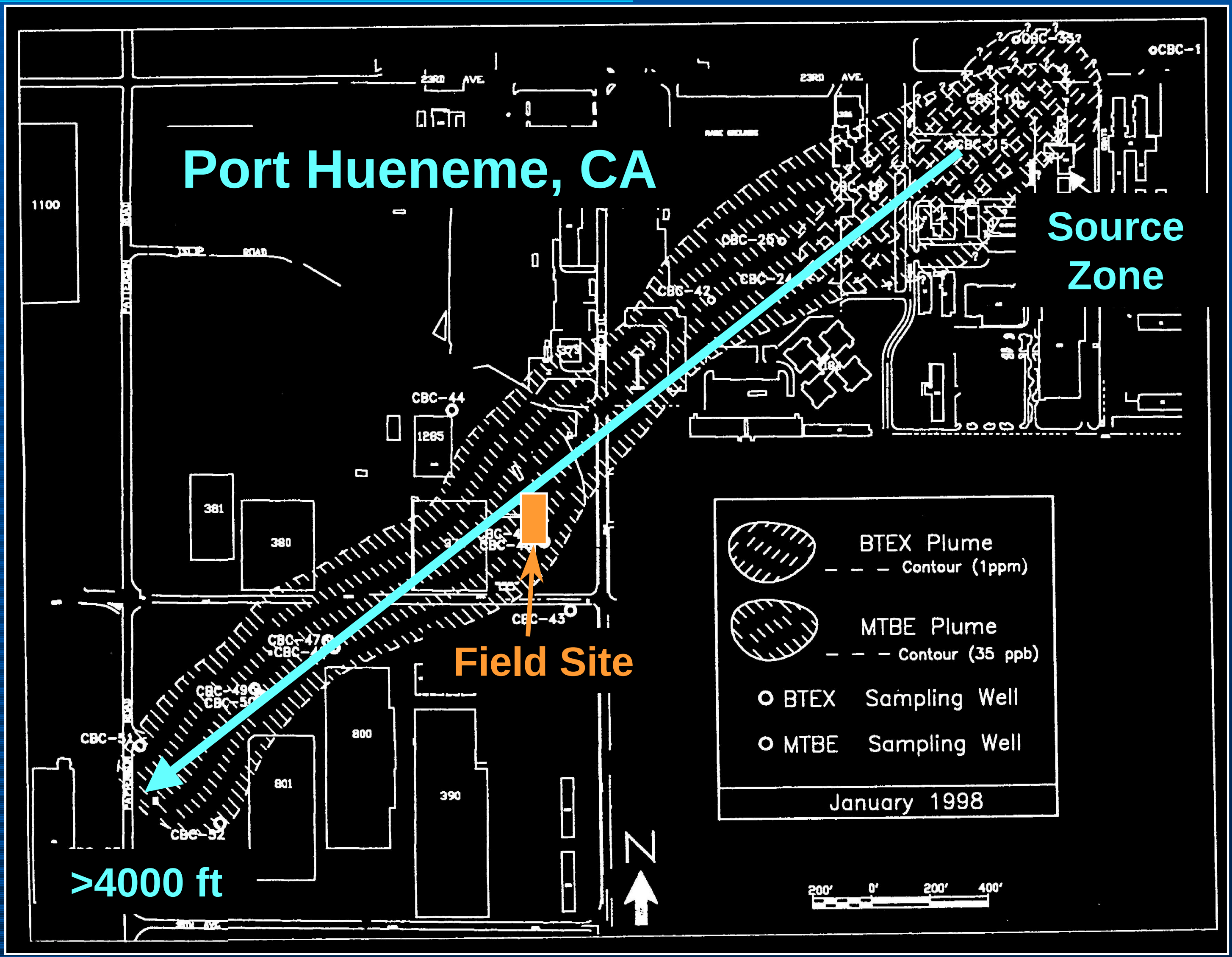
Case Study: Biobarrier Field Test, Port Hueneme, CA

- Conducted at the NCBC Port Hueneme, CA
- MTBE Plume >4,000 ft long
- Treatment plot situated in MTBE-only portion of the plume
- MTBE concentrations in this area range from 2 to 9 mg/L
- DO concentrations are <1 mg/L in this area
- Depth to water is approximately 10 ft, and MTBE plume is 10 ft thick

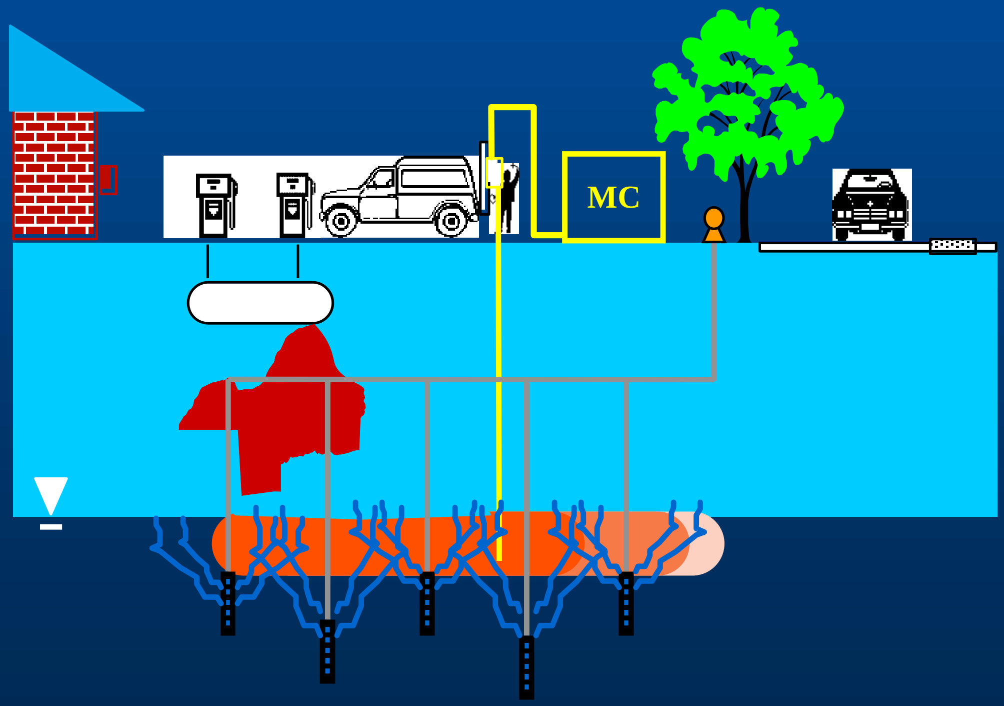
Case Study: Biobarrier Field Test, Port Hueneme, CA



Case Study: Biobarrier Field Test, Port Hueneme, CA

- This enhanced biodegradation technology involves three main steps:

1) Oxygenate (by pure oxygen injection)
2) Inoculate with MTBE-degraders (MC-100)
3) Monitor



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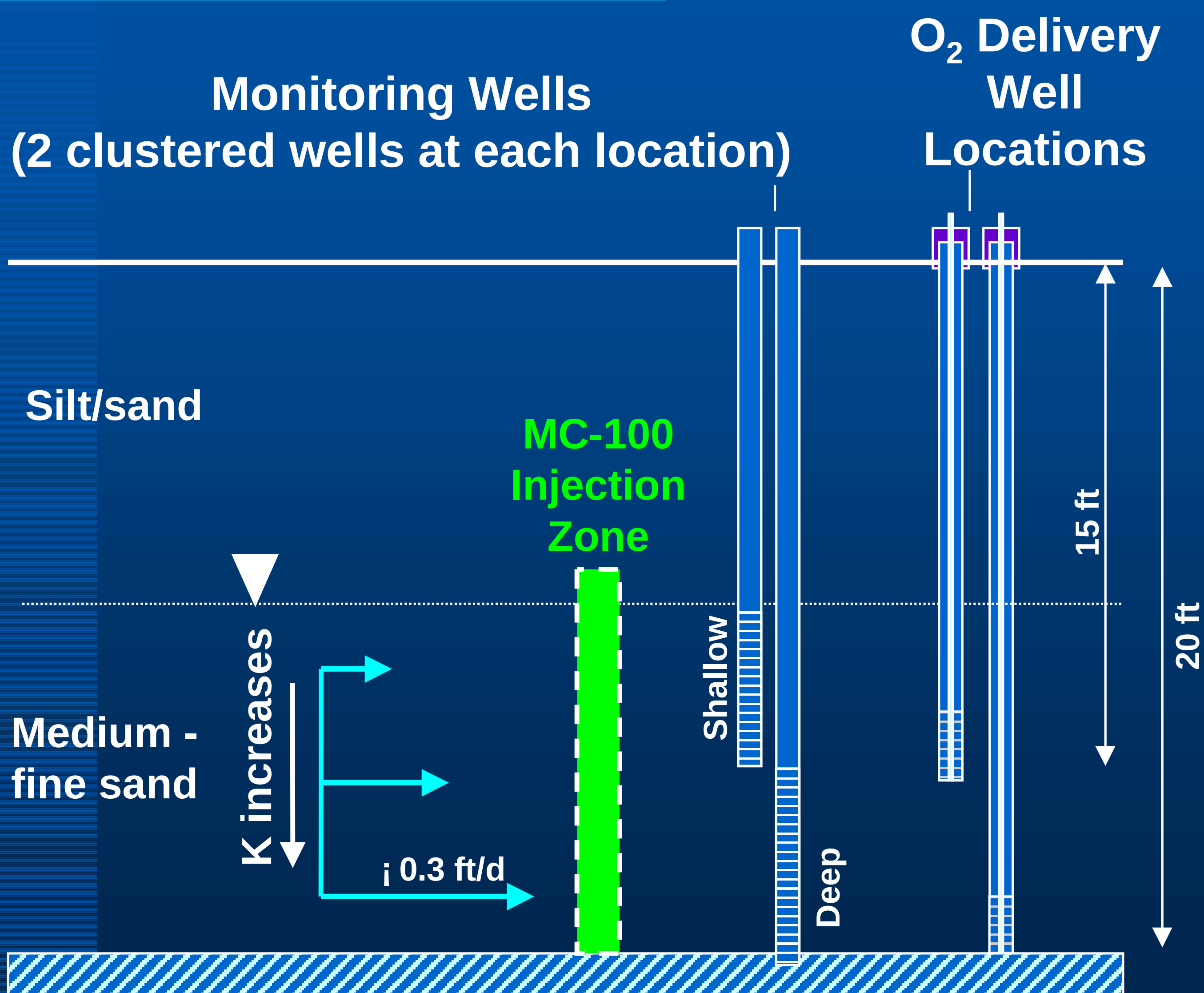
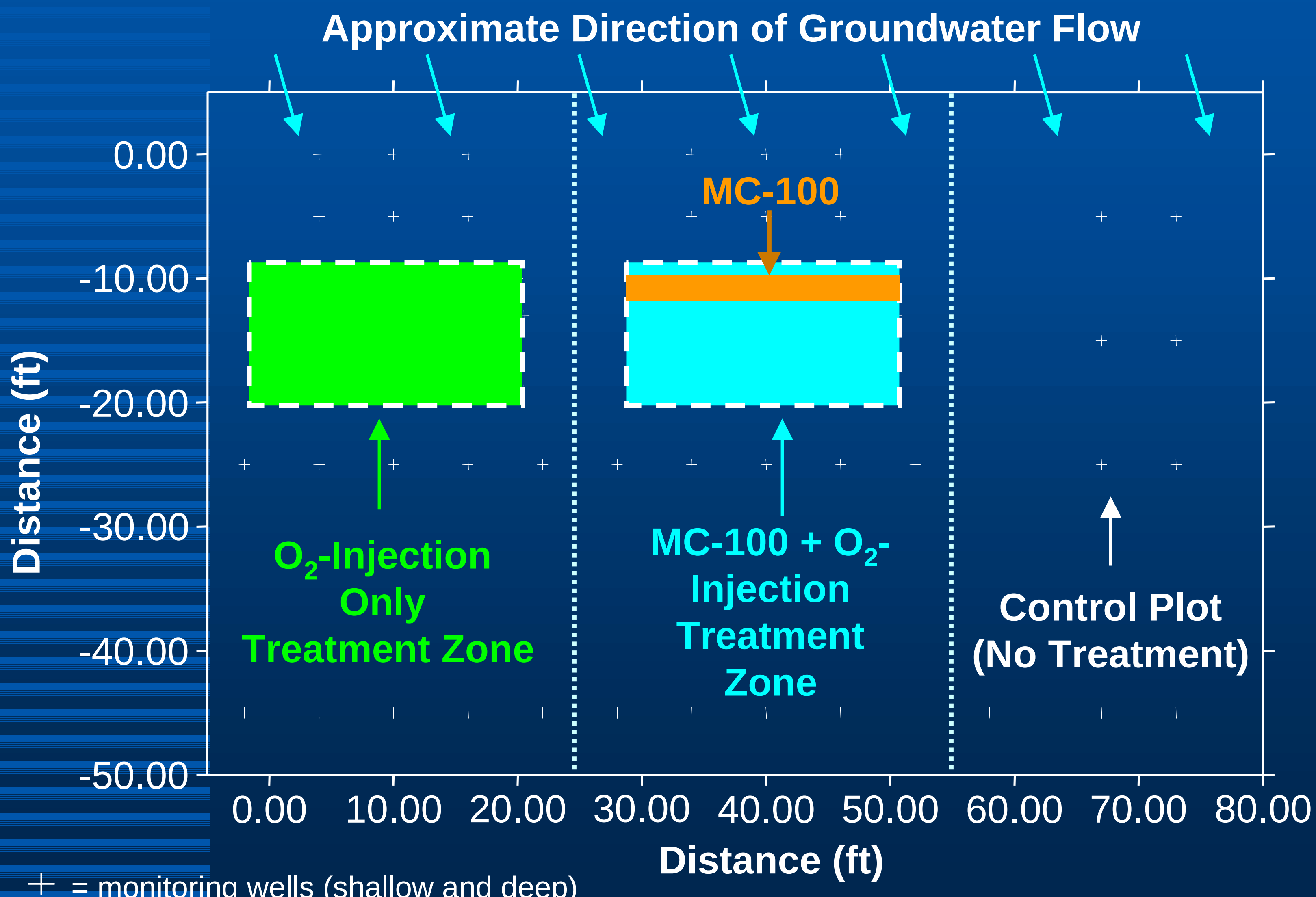
Case Study: Biobarrier Field Test, Port Hueneme, CA
Biobarrier – Subsurface Features



Case Study: Biobarrier Field Test, Port Hueneme, CA

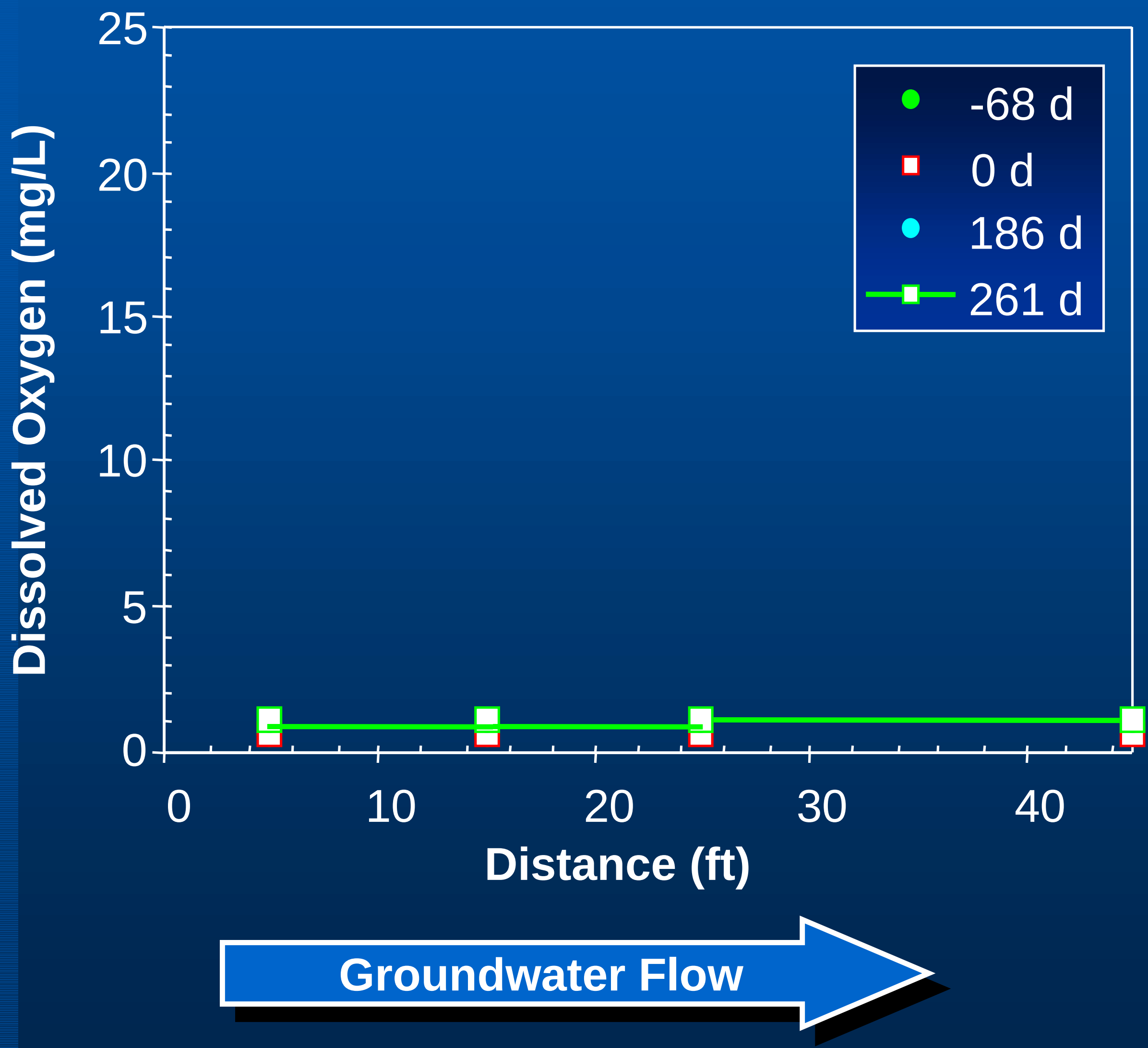
Biobarrier – Field Test Layout



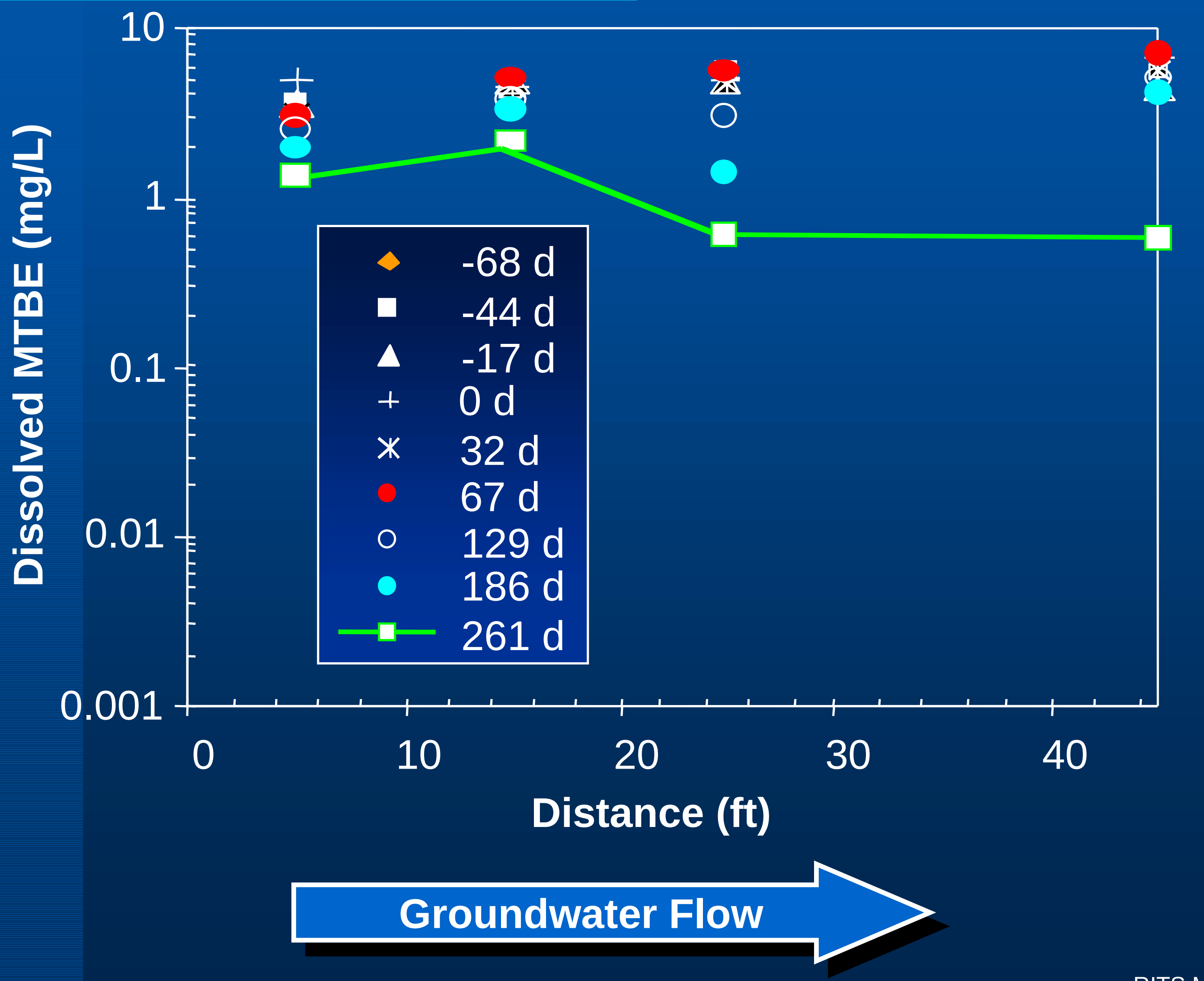
Case Study: Biobarrier Field Test, Port Hueneme, CA

Case Study: Biobarrier Field Test, Port Hueneme, CA

Control Plot (Shallow)

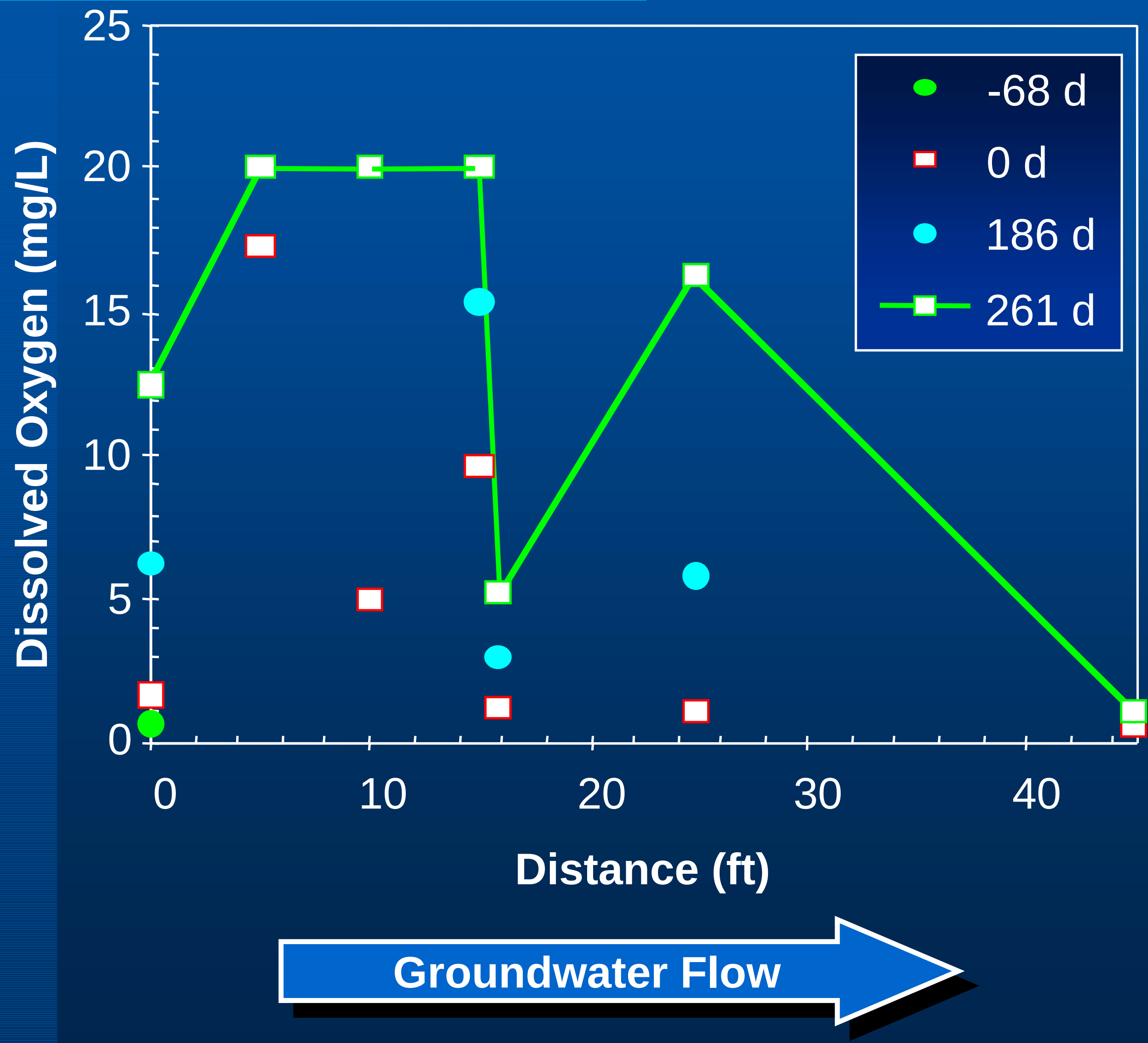


Case Study: Biobarrier Field Test, Port Hueneme, CA
Control Plot (Shallow)



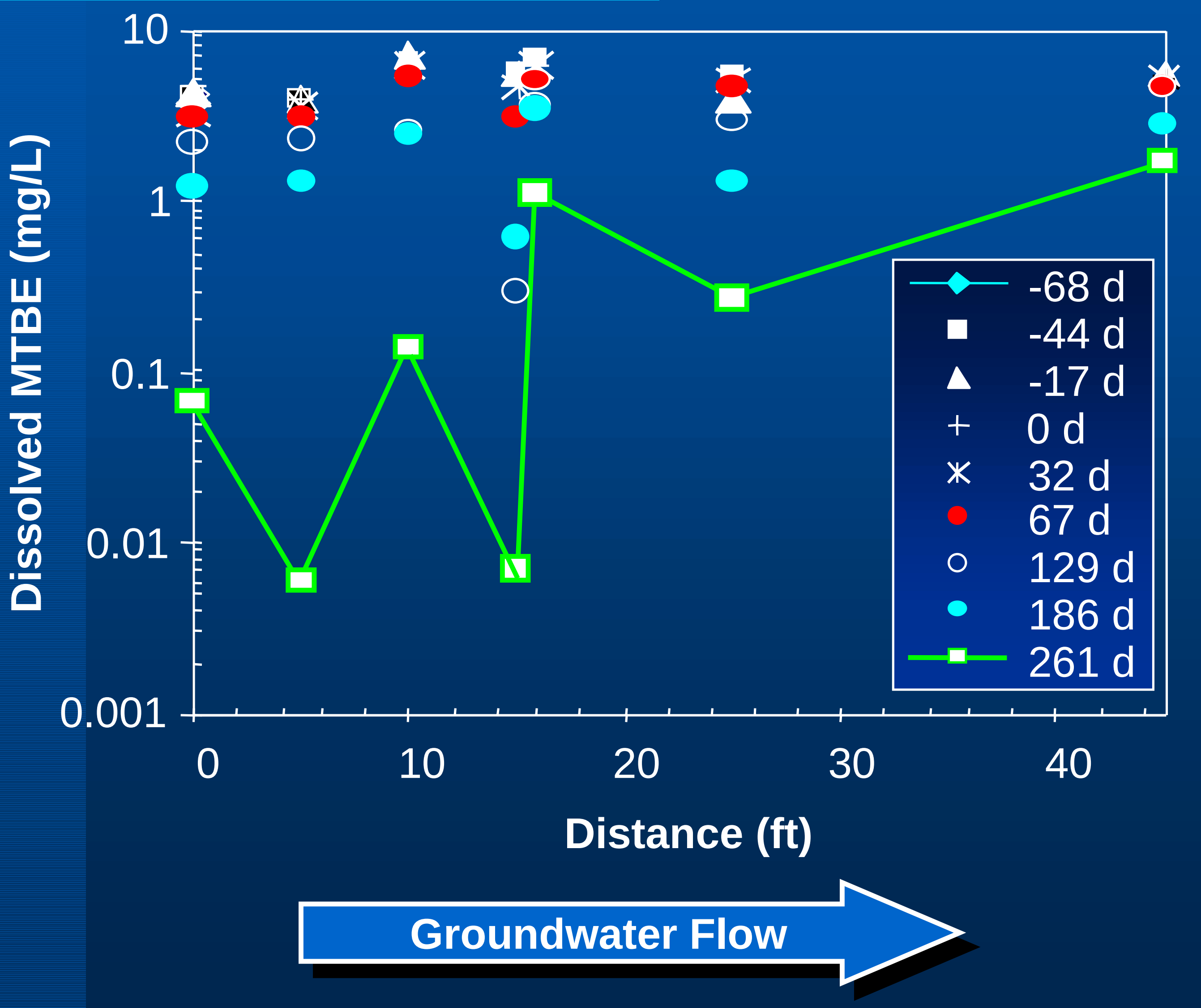
Case Study: Biobarrier Field Test, Port Hueneme, CA

O_2-Injection Only Plot (Shallow)



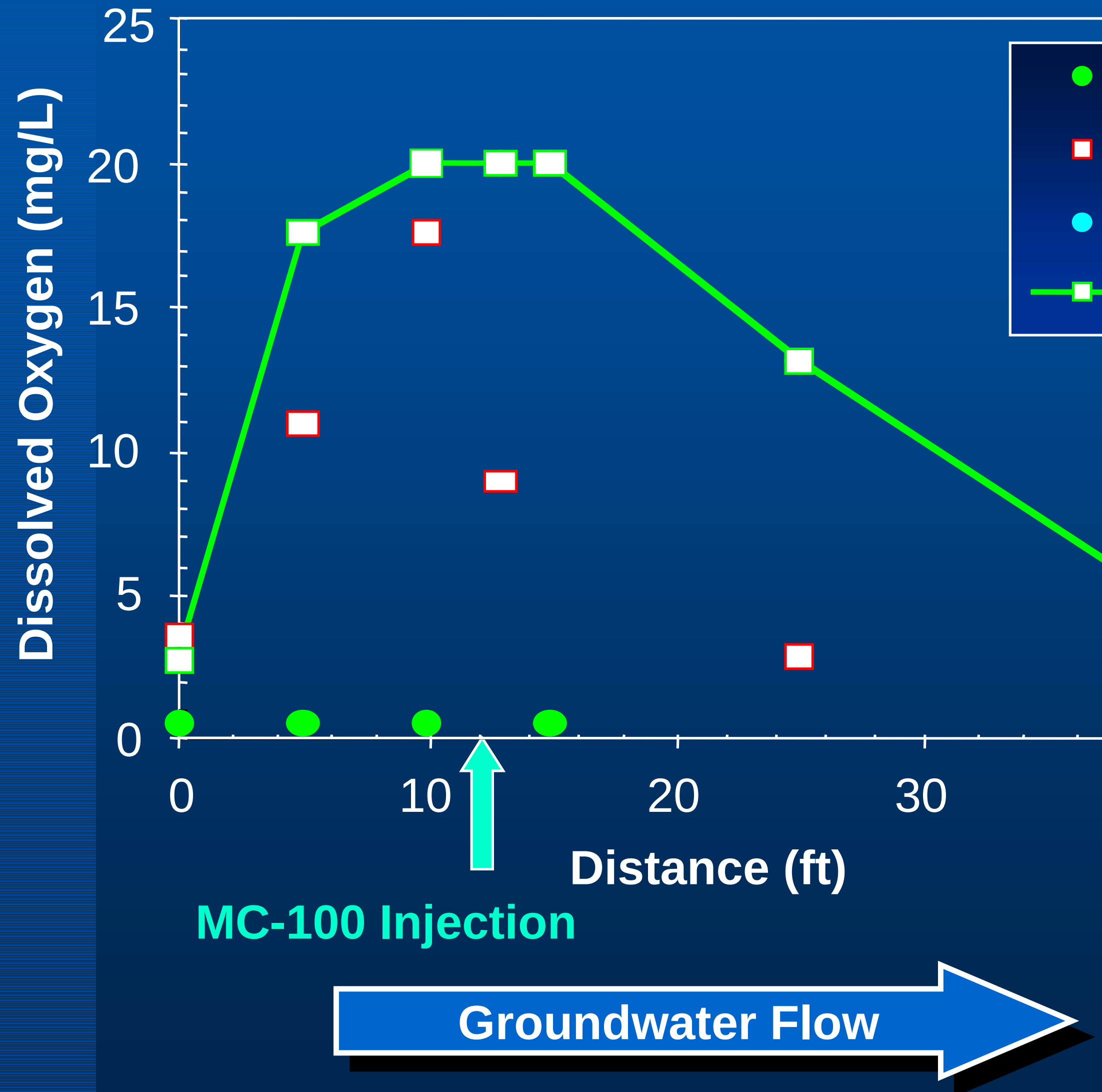
Case Study: Biobarrier Field Test, Port Hueneme, CA

O_2-Injection Only Plot (Shallow)



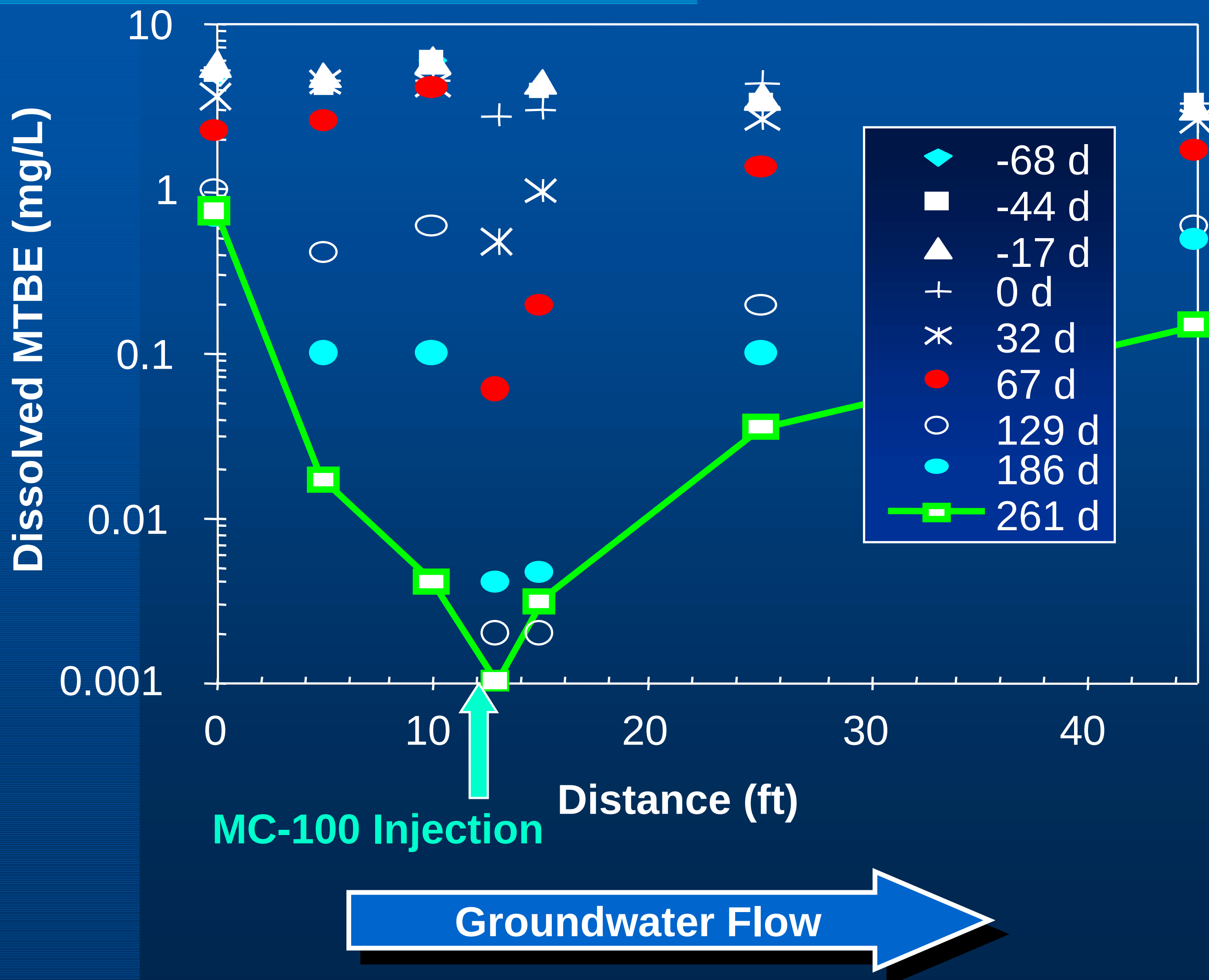
Case Study: Biobarrier Field Test, Port Hueneme, CA

MC-100 and O_2-Injection Plot (Shallow)



Case Study: Biobarrier Field Test, Port Hueneme, CA

MC-100 and O_2-Injection Plot (Shallow)



Case Study: Biobarrier Field Test, Port Hueneme, CA

Results

- Intermittent pure oxygen sparging started 6 weeks before microbial seeding; raised DO levels from about 1 mg/L up to 10-20 mg/L
- 32 days after seeding with MC-100 (aka BC-4), MTBE levels immediately downgradient dropped 90% (no change yet in the control or oxygen-only plots)
- By day 261 MTBE in the treated plot was ND in many sample locales, with 10-50 µg/L in a few locales
- By day 261, the O_2-only plot did show MTBE decreases; apparently enhanced natural process after some lag time

Case Study: Biobarrier Field Test, Port Hueneme, CA

Summary and Conclusions

- Some biostimulation due to oxygen injection alone, but it is less effective than with MC-100, and there is lag time
- At this time, augmentation appears to be necessary for in situ MTBE biotreatment
- In situ MC-100 biobarrier appears to be capable of degrading MTBE to <5 μg/L, w/out TBA residuals (and activity remains to at least 261 days)
- The combination of bioaugmentation with oxygen addition appears to be a feasible in situ MTBE biotreatment option

Case Study: La Crosse, KS
Site History

- La Crosse, KS is a small rural farming community of approximately 1,500 people
- Public water supply is from several production wells, in a sole-source aquifer; wells are screened 50 to 70 ft below grade
- In May 1996, a resident noticed a strange odor in an irrigation well

Case Study: La Crosse, KS
Site History

- Sampling of adjacent public well detected MTBE at 200 µg/L; concentration later reached a maximum of 600 µg/L
- MTBE was from a gasoline spill at a co-op service station in the early 1990's; volume unknown
- Later detailed assessment (using 60 monitoring wells) showed that MTBE had migrated beneath the 800-foot-long, two-dimensional (2-D) shallow monitoring system, entered the valley-fill aquifer, and impacted the well field 4,000 feet away!

Case Study: La Crosse, KS

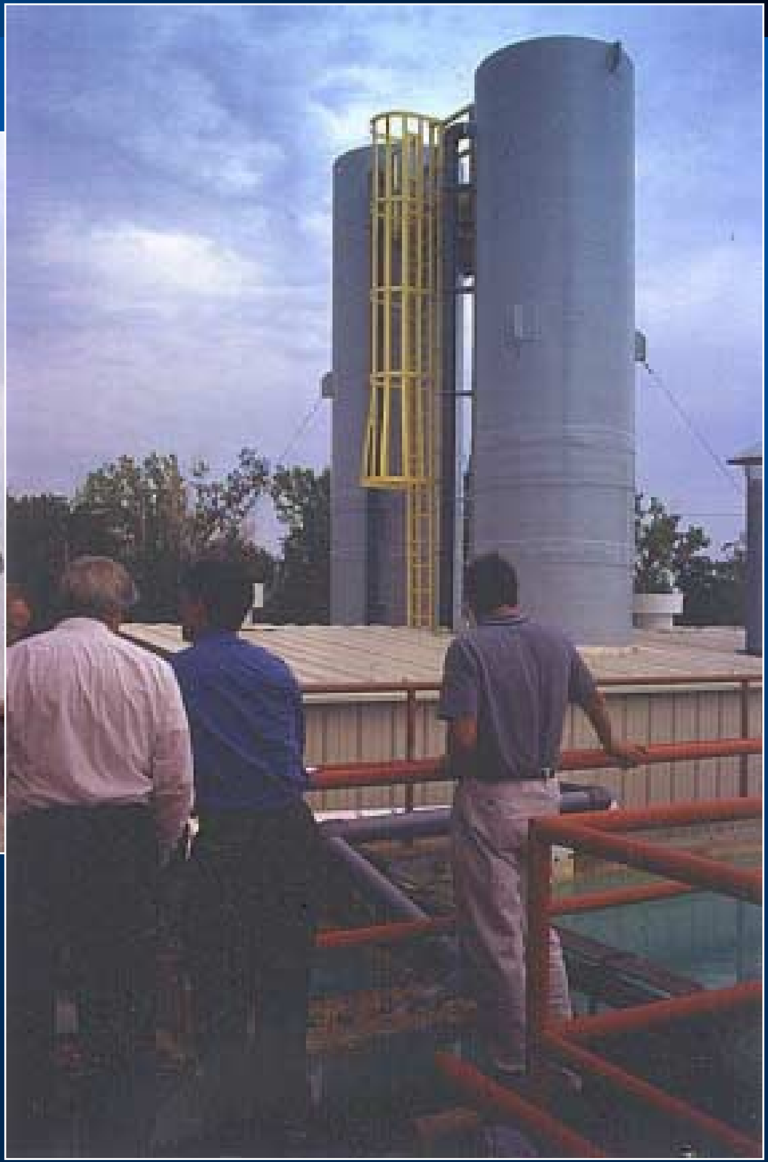
Case Study: La Crosse, KS
Remediation System

- Two impacted public wells were pumped at total flow rate of 300 gpm (winter) to 450 gpm (summer) to contain and extract contaminated groundwater
- Source-area remediation techniques implemented:
  - Limited soil excavation
  - AS/SVE system installed; limited effectiveness due to low permeability layer just above the water table
  - ORC barrier injected at mid-plume; effectiveness unknown

Case Study: La Crosse, KS
Temporary Treatment System

- An undersized shallow-tray air stripper was readily available. As an emergency system, water extraction reduced to 250 gpm, and available stripper installed. Removal efficiency averaged 40%.
- Public concern very low; no taste and odor complaints before, or after (water is quite hard).
- Treated water served to public with 80 to 300 µg/L of MTBE (no BTEX).

Case Study: La Crosse, KS



Case Study: La Crosse, KS
Permanent Treatment System

- In September 1997, two air strippers installed at water treatment plant
- Each was 35 feet tall, 6 feet in diameter, with 30 feet of 2-inch Jaeger tripacks
- Strippers operated in series, each with air:water of 175:1
- No off-gas treatment required
- Each tower achieves about 90% removal (80% in winter)
- With influents of 200-600 µg/L, treated water ranges from ND – 24 µg/L
- Treated water served to public for more than 2 years now

Case Study: La Crosse, KS
Summary and Conclusions

- Spill history unknown, but aquifer impacted by MTBE-blended gasoline sometime in last 10 years
- Typical 2-D plume definition missed the deep MTBE plume
- Source area remediation fair at best
- Impacted supply wells used to contain plume at low cost
- Two air strippers in series used to treat water, with a total of 96 to 99% MTBE removal
- Simple and logical application of traditional technologies restored water usage; water currently is being served to public
- MTBE remediation and treatment can be done!

Select References: Chronological Order

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